Determination of Triethylamine in Air by Flow-injection Chemiluminescence

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***Abstract*-A novel flow-injection chemiluminescence (CL) method for the determination of triethylamine had been established in this study. Based on the chemiluminescence reaction between triethylamine and sodium hypochlorite in alkali condition, the fluorescein has strong sensitization in this chemiluminescence reaction. Under the optimized conditions of chemiluminescence reaction, FI parameters and the absorbing efficiency of triethylamine in the air, the enhanced intensity of chemiluminescence was proportional to the concentration of triethylamine in the range of 0.001～0.10g/L, and the relative standard deviation was 0.89% (n=11) at 0.05g/L triethylamine. The detection limit was 0.8mg/L in aqueous. The proposed method had been applied successfully to determine triethylamine in the lab air.**

Keywords-flow-injection; fluorescein; triethylamine; sodium hypochlorite; chemiluminescence

I. INTRODUCTION

Amines have been considered as the second most harmful substance for water pollution and environment in addition to organic sulfide. For these reasons, amines have recently strongly attracted the sight of the environmentalists both domestic and foreign. The common basic aliphatic amines include methylamine, ethylamine, isopropylamine, butylamine, trimethylamine, and triethylamine[1-2]. Triethylamine (N, N-diethyl-ethanamine) is transparent liquid with the structure of aromatic amines and the foul smell of ammonia. Triethylamine is one of the components of liquid rocket propellant. It is widely applied in many industrial productions, such as dyes, rubber vulcanization agent, pesticides, pharmaceuticals and industrial solvent. For the widely producing and use in industry, triethylamine has been found in natural environment and water. Scientists has studied that human body prolonged exposure in the environment of triethylamine will lead to such as vertigo, nausea, cough, shortness of breath, blurred vision, abnormal bone marrow chromosomes structure and so on. Therefore, triethylamine has been suspected to cause cancer and distortion. Considering the harm of triethylamine mentioned above, the government has established a reference concentration standard of triethylamine of 2 mg/L in water for living and drinking in National Standards of the People's Republic of China GB 2001.

Thereby, determination of triethylamine in environment has aroused great attention by public. Nowadays, various analytical methods have been reported for the determination of triethylamine [3-9], with distinctive features respectively, e.g., gas chromatography, spectrophotometry, fluorescence-spectrophotometry, ion chromatography, liquid chromatography, Electrochemiluminescence and so on. In this work, a new CL flow system for the determination of triethylamine based on the sensitizing effect on the CL reaction of alkaline sodium hypochlorite and fluorescein is proposed. In the optimized conditions, the enhanced intensity of chemiluminescence responsed linearly to the concentration of triethylamine.

II. EXPERIMENTAL

A. *Instrumentation and Reagents*

IFFM-E chemiluminescence instrument and IFFS-A chemiluminescence detector (Remex, Xi'an city, China); DQ-1 air sampler.

Stock solution of triethylamine: 0.1g/L; Solution of sodium hypochlorite (NaClO): 0.24g/L; Solution of fluorescein: 6×10^{-4} mol/L; Solution of sodium hydroxide (NaOH): 0.03mol/L.

B. *Experimental Procedure*

The schematic diagram of chemiluminescence analysis is demonstrated in Fig. 1. Three flow channels a,b,c load NaClO solution, alkaline fluorescein solution and triethylamine solution, respectively. A stable baseline will be achieved by washing the flow system with each solution at a constant velocity. Both NaClO solution and alkaline fluorescein solution are injected into the flow cell, subsequently mixing with reagent stream (triethylamine solution) to give CL signal, which is recorded by a sensitive photomultiplier tube. The content of triethylamine in the sample is quantified by the relative CL intensity △I=IS－I0, where is and I0 are the CL-signals in the sample (sample solution with fluorescein and NaClO) and blank (redistilled water with fluorescein and NaClO). The enhanced intensity of chemiluminescence (△I) is theoretically proportional to the concentration of triethylamine.

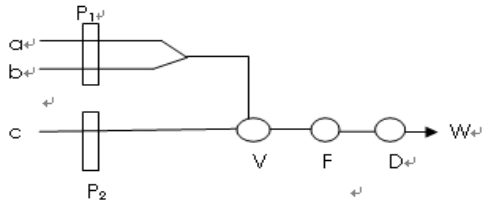

Fig.1 Schematic Diagram of Manifold of the Flow Injection Chemiluminescence Analysis

a: NaClO b: fluorescein+NaOH c: triethylamine P_1、P_2: peristaltic pump V: injection valve F: flow cell D: detector W: waste solution

III. RESULTS AND DISCUSSION

A. *Optimization of the Flow-Path*

It has a very strong influence on the CL emission with different mix orders of reactants. So, the effect of six different mix orders of reactants including {NaClO+ triethylamine}+{fluorescein+NaOH};{NaClO+fluorescein}+{triethylamine+NaOH)};{NaClO+NaOH)}+{fluorescein+triethylamine};{NaClO+triethylamine}+(fluorescein+NaOH);{NaClO+(fluorescein+NaOH)}+triethylamine;NaClO+{triethylamine+(fluorescein+

NaOH)} on the CL intensity was studied. The results showed that the maximum CL signal was achieved in the fifth mix order. So, the fifth mix order: {NaClO+ (fluorescein+ NaOH)} + triethylamine was used throughout for subsequent work.

B. Optimization for CL System

1) Effect of NaClO Concentration

The impact of different concentrations of NaClO on CL intensity was investigated in the range of 0.15g/L ~ 0.30g/L for 0.1g/L triethylamine. It is observed that the CL intensity was significantly enhanced along with the increasing concentration of NaClO, whereas decreasing over the0.24 g/L NaClO. Thus, 0.24 g/L NaClO solution was chosen as the optimum.

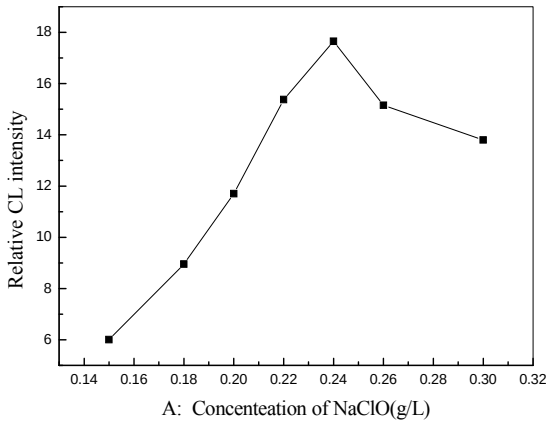

Fig.2. Effect of Naclo Concentration on the CL Intensity
NaOH: 0.1mol/L ; Fluorescein: 1×10^{-3}mol/L ;
Triethylamine: 0.1g/L; Temperature: 20℃～25℃

2) Effect of Temperature

Temperature is also considered as a key factor influencing the CL emission intensity. Therefore, the dependence of the CL intensity on temperature in range of 8 ～ 25℃ was investigated for 0.1g/L triethylamine. The Fig. 3 showed that the CL intensity increased with the increasing temperature. As shown, when the temperature was over 21℃, the CL intensity only had very stable response. Therefore, the optimized temperature was selected to be 20～25℃for further studies.

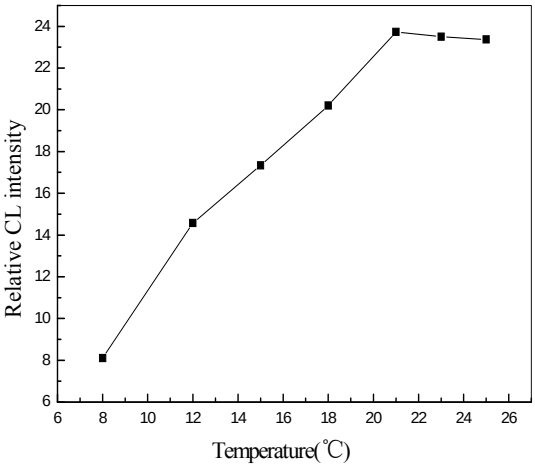

Fig.3. Effect of Temperature on the CL Intensity
NaOH: 0.1mol/L ; Fluorescein: 1×10^{-3}mol/L ;
Triethylamine: 0.1g/L; NaClO: 0.24g/L

3) Effect of NaOH Concentration

This chemiluminescence reaction was conducted in alkali condition; hence the concentration of NaOH had significant influence on the CL intensity. A study of this influence was carried out over the NaOH concentration range of 0.02mol/L to 0.06mol/L under the standard conditions mentioned above and the results are given in Fig. 4. Examination of this figure shows that the maximum intensity was obtained at the NaOH concentration of 0.03mol/L. When the NaOH concentration was above this level, the CL intensity decreased sharply. Thus, 0.03mol/L NaOH was chosen for consequent research.

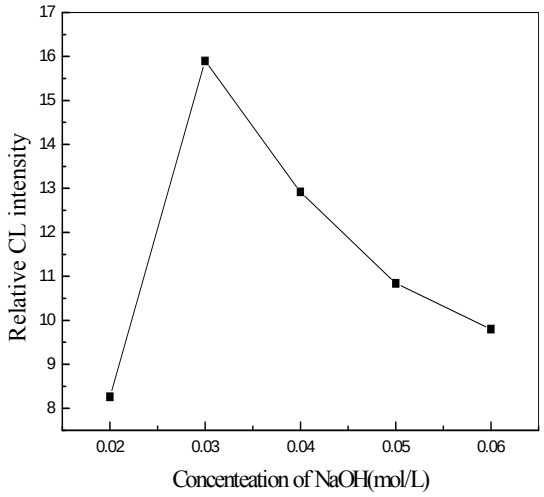

Fig.4. Effect of NaOH Concentration on the CL Intensity
NaClO: 0.24g/L ; Fluorescein:1×10^{-3}mol/L ;
Triethylamine: 0.1g/L; Temperature: 20℃～25℃

4) Effect of Sensitizers

In order to investigate sensitizers' potential effects on present CL reaction, a few different fluorophores were selected and examined in this study, such as fluorescein, rhodamine B, ethylrhodamine B and sodium dodecyl benzene sulfonate(SDBS). It was found that fluorescein can greatly enhance the CL generated by the reaction of NaClO with triethylamine in alkali condition (see Table 1).

Therefore, fluorescein was used as sensitizer for further investigation. The effect of fluorescein concentration in the range $0\sim1.0\times10^{-3}$ mol/L was investigated (Fig.5). The CL intensity increased with the increasing concentration of fluorescein up to 6.0×10^{-4} mol/L; and above the concentration of 6.0×10^{-4} mol/L, the CL intensity declined probably because of absorption of light by fluorescein at higher concentrations. Hence, the optimized fluorescein concentration was selected to be 6.0×10^{-4} mol/L for further studies.

TABLE 1 EFFECT OF SENSITIZERS ON THE CHEMILUMINESCENCE INTENSITY

Sensitizer	**Concentra (10^{-4}mol/L)**	**CL intensity**
fluorescein	10	24.35
rhodamine B	10	7.84
ethylrhodamine B	10	10.02
SDBS	10	6.97

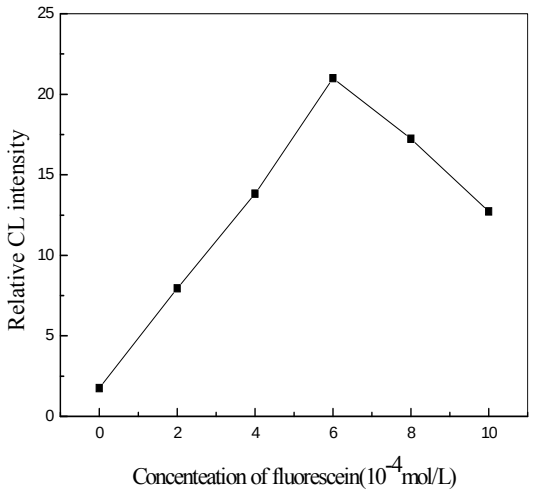

Fig.5. Effect of Fluorescein Concentration on the CL Intensity
NaOH: 0.1mol/L ; NaClO: 0.24g/L ;
Triethylamine: 0.1g/L; Temperature: 20℃～25℃

C. Optimum FI Parameter Condition for CL System

1) Effect of the Pump Speed

The pump speed will affect the CL emission intensity. The effect of the pump speed on the CL intensity of the system was studied over the range of 60~ 99 r/min under the standard conditions mentioned above in order to improve SNR (Signal to Noise Ratio), and the result shows that the CL intensity increased with the increasing pump speed. Thus, a pump speed at 90r/min was chosen for further studies considering reagent cost and diminishing instrumental wastage.

2) Effect of the Hybrid Tube Length

Hybrid tube is a mixed pipe where two reaction solutions mix before flowing into the sampling ring. In this study, the length of the hybrid tube has shown positive effect on the CL intensity, which indicates. The CL intensity increases with the length of the hybrid tube, and the maximum intensity was obtained at the hybrid tube length of 14 cm. Therefore, the length of 14 cm was chosen for consequent research.

3) Effect of the Reaction Tube Length

The Reaction mixture flows from sampling ring into flow cell through reaction tube, thereby the length of reaction tube affects, to some extent, the mixability and the CL emission intensity. The CL intensity increased with increasing reaction tube length up to 23cm; and above 23cm, the CL intensity declined Therefore, the optimum reaction tube length was selected to be 23cm for further studies.

4) Effect of Injection Volume

The injection volume of sample influences the CL emission intensity. It was investigated for 0.1 g/L triethylamine in the range 50μL～150μL(Minimum volume is 50μL, limited by the instrument performance), the results showed that the CL intensity increased with the increasing injection volume up to 100μL; and above100μL, the CL intensity only had very minor increase. Therefore, 100μL injection volume was chosen as optimum.

5) Influence of Sampling Time

The sampling time is an important factor for sample collection capacity. By exploring the relationship between the sampling time and the CL signal, we found that the CL system can get stable baseline with high sensitivity while the sampling time up to 6s. So we choose 6s as the optimized sampling time in this experiment. In the meantime, -800 volt is selected to be the optimum negative high voltage.

D. Analytical Characteristics

Under the optimum conditions determined above, the calibration graph of the emission intensity (I) versus the triethylamine concentration was linear over the range 0.001~0.1g/L and the regression equation was △I=1.3509C+0.299 (0.001~0.01g/L) with a correlation coefficient of 0.9972;△I=0.2441C+10.489(0.01~0.1g/L) with a correlation coefficient of 0.9983(C: triethylamine concentration, g/L). The detection limit was 0.0008 g/L. The relative standard deviation for 0.05 g/L triethylamine was 0.89% for 11 repetitive analyses.

E. Tolerance of Interfering Impurities

The influence of various impurities on the determination of 0.05 g/L triethylamine was investigated based on the tolerance limit for maximum concentration of impurities, controlling the measurement error within 5%. The foreign substances tolerated ratio to 0.05 g/L triethylamine was 1400 for formaldehyde, 800 for Hexamethylene Tetramine (HMTA), 160 for Ni^{2+}, 100 for diethanolamine (DEA) and ethylenediamine, 40 for Zn^{2+}, 10 for Cu^{2+}, and 6 for Fe^{3+}. We can find that Zn^{2+}, Cu^{2+}, Fe^{3+} will interfere with the determination of triethylamine so that these metal ions need to be eliminated. However, EDTA can improve the multiple coexisting of metal ions so we add 0.3 mg sodium fluoride as the masking agent in place of EDTA which could be precipitated with Fe^{3+}.

F. Optimization of Absorption Condition

1) Influence of Absorption Solution

The choice of absorbing solution has a great impact on sampling result, sampling time and efficiency. We choose acid solutions as absorbing solution because organic amines are normally alkaline. So, various acid such as citric acid ($C_6H_8O_7$), sulfuric acid (H_2SO_4), tartaric acid ($C_4H_6O_6$), acetic acid (CH_3COOH) and phosphoric acid (H_3PO_4) were introduced as absorption solution and investigated in the same sampling conditions (sampling time and experiment environment) with the same concentration of 0.1mol/L. By comparing the intensity of CL, it is obvious that HNO_3 and H_2SO_4 give the higher CL signal. Because of the strong causticity of H_2SO_4, H_3PO_4 was finally chosen as the absorbing solution for our consequent research. The concentration of H_3PO_4 was subsequently optimized and the results were shown in table 2. The higher concentration of H_3PO_4 corresponded to higher CL signal intensity, and the signal reached its peak at the concentration of 0.05mol/L. then declined. Thus, the optimum H_3PO_4 concentration was selected to be 0.05mol/L in our subsequent work.

TABLE 2 INFLUENCE OF H_3PO_4 CONCENTRATION ON THE SAMPLING EFFECT

Concentration of H_3PO_4 (mol/L)	Relative CL intensity △I
0.01	13.8
0.03	17.6
0.05	19.4
0.08	18.2
0.1	17.4

2) Determination of Absorption Time

A suitable absorbing time is another important factor which can influence the experiment results directly. Short absorption time which lead to little material be measured will give rise to no result. On the contrary, too long time may introduce too much impurity, leading to metamorphism of the absorption sample. A study of this factor was carried out over the absorbing time of 60min, 90min, 120min, 150min and 180min in the standard conditions mentioned before. We find that the maximum CL signal intensity was achieved after 120min, and the absorbing time has little influence on the signal above this level. Considering the laboratory schedules, 120min is a suitable absorbing time for our further studies.

3) Influence of Sampling Flow Rate

A proper sampling flow rate which can influence the magnitude of the sample collection directly is important. The samples were collected at a series sampling flow rates of 0.1L/min, 0.3L/min, 0.5L/min,0.8L/min were determined. From the results, we can find that the CL signal increased with higher flow rate. Considering the signal to noise ratio of the system and to diminish instrumental wastage, the optimal sampling flow rate was determined to be 0.5 L/min in further studies.

IV. SAMPLE ANALYSIS

Based on the method of air collection and chosen sampling absorption conditions, an appropriate volume of air samples of laboratory of CLA-B303 and CLA-B404 and reagent room were collected by DQ-1 air-sampler. Adjusted the pH of the sample to 9.5 with 1mol/L NaOH and diluted it to 50mL with redistilled water in 50mL colorimetric cylinder. The concentration of three laboratory samples and the reagent blank were determined by the present system. The recovery test for the developed procedure was performed (n=3). All the results were shown in table 3.

The recovery rate of the Lab 2 sample is not between 95%~105%. The possible reason of this case is the interference of the organic amines and other matters in the air.

TABLE 3 DETERMINATION OF TRIETHYLAMINE IN SAMPLE SOLUTION

Sample	Found (μg)	Added (μg)	Recovered (μg)	Recovery (%)
Lab 1	2.08	3.0	5.18	103.3
Lab 2	3.26	4.0	7. 64	107.5
Lab 3	2.01	2.0	3.94	96.5

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